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GB A 2164357 GB 1291357 EP A1 0091998
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(54) Cadmium sulphide solar cells

(57) A method of forming a cadmium sulphide deposit on a transparent substrate, which may be glass having a transparent layer of tin oxide, comprises spraying a suitable precursor solution onto the substrate and heating the substrate to evaporate the droplets of precursor on the substrate, by resting the substrate 26 as illustrated in Fig. 1, on a ceramic plate 24 heated at least from beneath by tungsten halogen filament bulbs 22 serving as heating elements. The product finds use as a solar cell and to reduce the resistance of the cadmium sulphide layer indium may be introduced into this layer.

A method of forming a copper sulphide/cadmium sulphide heterojunction which comprises immersing the cadmium sulphide layer in an organic solution containing a copper salt, and exposing the surface to light radiation so as to stimulate the growth of a topotaxial layer of copper sulphide on the cadmium sulphide is also disclosed. In a preferred embodiment of producing this heterojunction a solution of cuprous iodide leads to the precipitation of copper iodide which then appears to undergo a solid phase reaction with the cadmium sulphide, thereby forming copper sulphide.

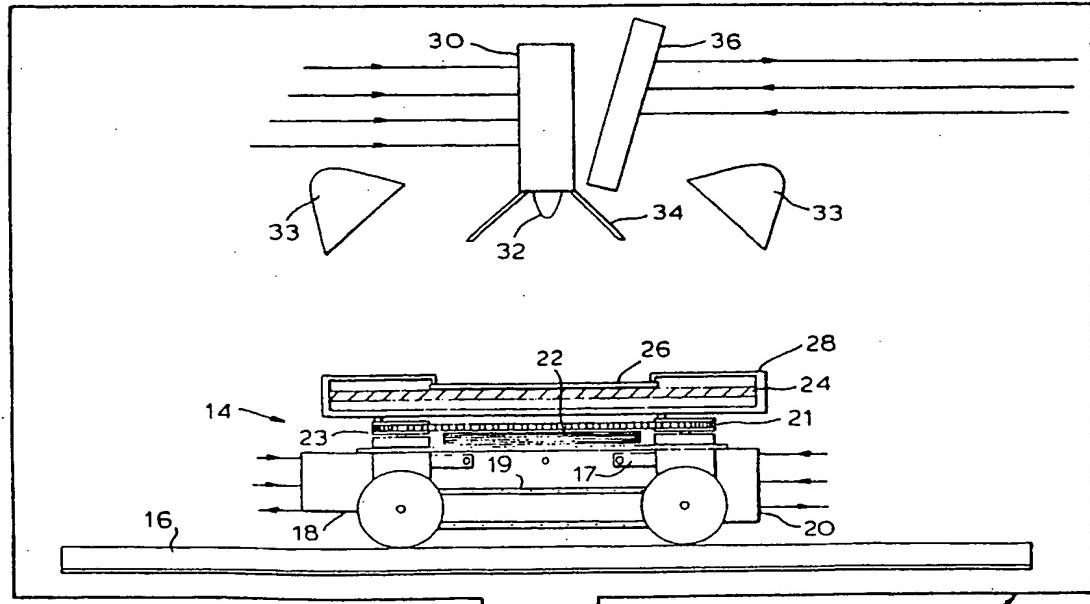
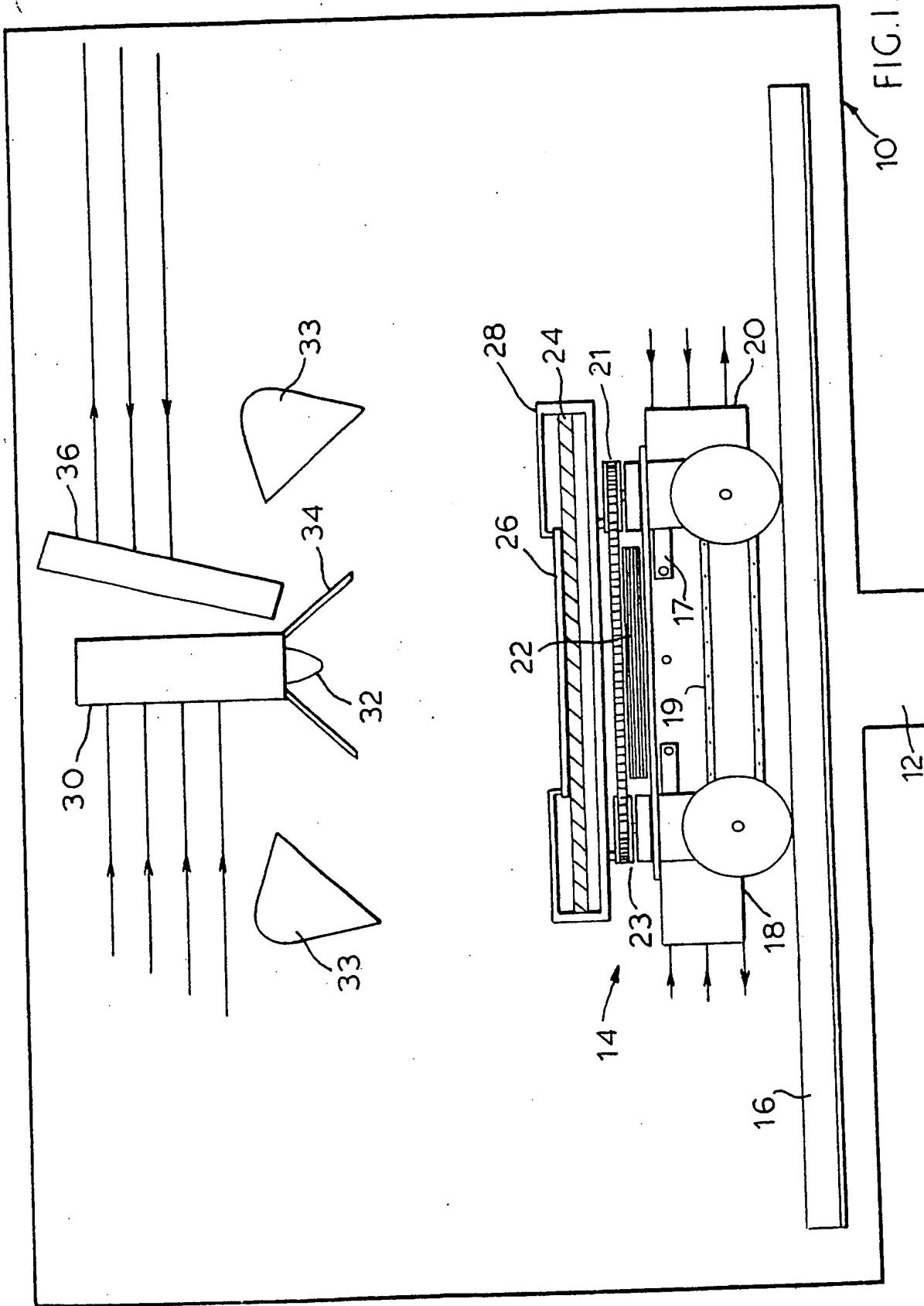


FIG. I.

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1-2



2-2

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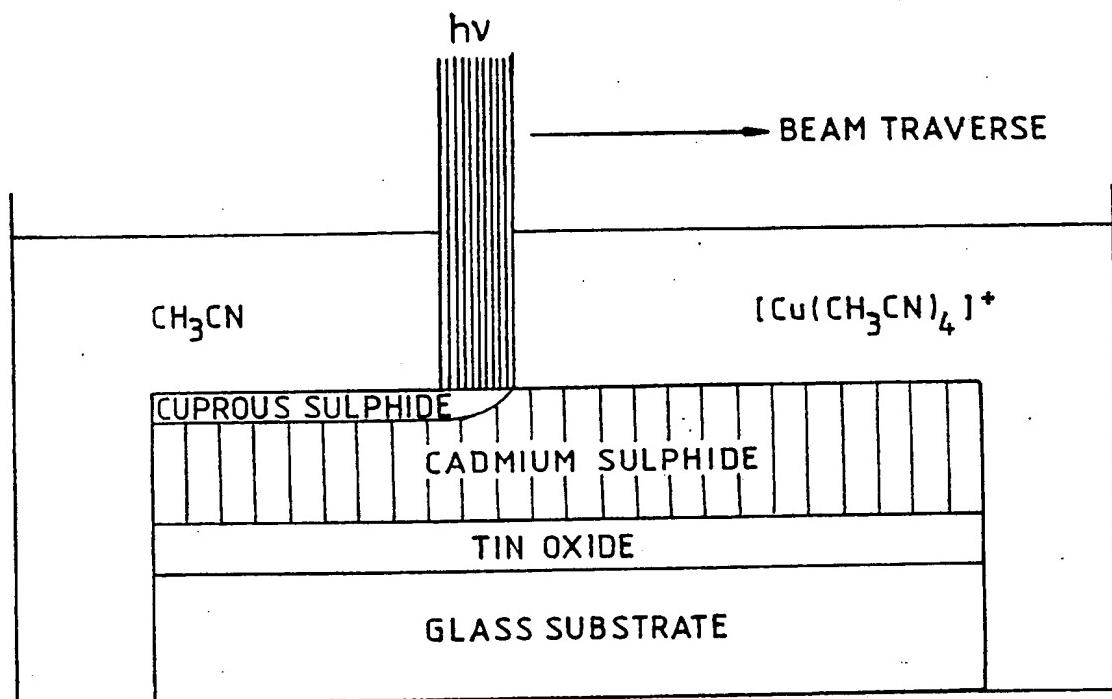


FIG. 2.

SPECIFICATION

Cadmium sulphide solar cells

5 The present invention relates to the manufacture of cadmium sulphide solar cells.

According to one aspect of the present invention, there is provided a method of forming a cadmium sulphide deposit on a transparent substrate, which comprises spraying a suitable precursor solution onto the substrate and heating the substrate to evaporate the droplets of precursor on the substrate, the substrate being heated by resting on a ceramic hob heated at least from beneath by tungsten halogen filament bulbs serving as heating elements.

Preferably the heating elements are elongate and are fitted with reflectors to direct the energy output onto the hob.

The rate of growth of the cadmium sulphide layer and the evenness of the layer are paramount considerations in the manufacture on a large scale of cadmium sulphide solar cells.

25 The growth rate is determined by the rate at which energy can be made to reach the surface of the substrate which is constantly being cooled by the spray of precursor solution. It has been found that the heating of the sub-

30 strate in the manner proposed in the present invention permits very high heat fluxes and correspondingly high deposition rates. Furthermore, the temperature can be maintained even over a substantial area, especially if the hob is moved over the heating elements following a circular or trochoidal path.

If desired, the substrate may additionally be heated by radiant energy directed onto the deposition surface from above.

40 The hob may be formed of the glass like ceramic material used in certain domestic hobs.

Advantageously, means are provided for measuring the surface temperature of the substrate and controlling the heating of the substrate to maintain the desired temperature.

To reduce the resistance of the cadmium sulphide layer it is possible to introduce small quantities of a dopant such as indium into the layer. This may be carried out after the layer has been formed but it is preferred to include an indium containing salt in the precursor solution.

After the cadmium sulphide layer has been 55 formed on a substrate, it is necessary to form a photoelectric junction with the cadmium sulphide by forming over it a layer of copper sulphide.

In accordance with a second aspect of the 60 present invention, there is provided a method of forming a copper sulphide/cadmium sulphide heterojunction which comprises immersing a cadmium sulphide layer in an organic solution containing a copper salt, and exposing 65 the surface to light radiation so as to

stimulate the growth of a topotaxial layer of copper sulphide on the cadmium sulphide.

Preferably, the light radiation is in the visible range and is produced by a laser. The laser 70 may conveniently be a carbon dioxide continuous laser and a beam produced by the laser may be scanned across the surface of the cadmium sulphide layer to stimulate the formation of the copper sulphide layer.

75 It is desirable to have high energy densities for the formation of the copper sulphide layer but excessive heating can give rise to problem on account of boiling. It may therefore be desirable to use the layer at high power but to 80 modulate its output, for example by rapid switching to allow time for the solution to cool between high energy pulses.

As an alternative, sunlight may be employed if focused onto the surface.

85 The sunlight or laser beam should be focused to a line extending across one dimension of the substrate and scanning may be effected either by deflecting the beam or by moving the substrate.

90 The invention will now be described further by way of example, with reference to the accompanying drawings, in which:

Figure 1 shows apparatus for the deposition of a cadmium sulphide layer, and

95 Figure 2 illustrates schematically the topotaxial growth of cuprous sulphide layer.

The apparatus in Fig. 1 comprises a stainless steel enclosure 10 which is vented to atmosphere through a port 12. Within the enclosure 10 there is provided a trolley 14 movable along a railway track 16. The trolley is fitted with heating elements in the form of tungsten halogen lamps 22 disposed beneath a support structure 28 carrying a ceramic plate 24 on which rests the substrate 26 to be coated with cadmium sulphide. The substrate 26 consists of a glass plate having a transparency need of course only be for the

100 wavelengths of light responsible for the photoelectric effect.

105 The trolley 14 carries two motors 18 and 20, the first to effect traverse of the substrate 26 and the second to rotate the substrate 110 during the deposition process. This movement is to assure evenness of exposure both to the heat from the heating elements 22 and to the spray from a spray head 30 fitted with an elliptical nozzle 32.

115 The mechanism for moving the substrate 26 during the deposition process includes a chain drive 19 for the traverse and a second chain drive 21 and bearings 23 for rotation of the ceramic plate. However, it is not deemed necessary to describe the displacement mechanism in detail within the present context as it is not fundamental to the invention.

120 Various lines are shown leading to the motors and to the trolley 14. These include lines 125 associated with position and temperature

130 associated with position and temperature

sensing and control lines for controlling the traverse and the rotation of the substrate.

The parts of the apparatus disposed above the trolley 14 include, in addition to the previously mentioned spray head 30 two further tungsten halogen lamps 33 an EHT electrode 34 surrounding the nozzle 32 of the spray head 30 and an optical pyrometer 36 arranged adjacent the spray head 30.

10 The lines leading to the spray head 30 represent the pneumatic control lines for emission control and the EHT (90 KV max) and also the supply lines for conveying the precursor solution to the spray head 30 and air for 15 protecting the pyrometer 36. Lastly, the lines leading from the pyrometer 36 represent an output line indicating the surface temperature and two supply lines conveying cooling water and gas for forming a nitrogen curtain.

20 Spray pyrolysis has been the subject of much investigation since it was first reported in 1966 by Chamberlin and Skarman (J. Electrochem. Soc. 113,86). Its use as a manufacturing technique for large area solar cells was 25 first suggested by J. F. Jordan in 1973 (Workshop Proc., Photo. Conv. Solar Energy Terr. Appl., Cherry Hill, p. 182) and it is an economic method for the deposition of semiconductor layers.

30 A majority of the work reported in the literature has employed conventional air atomisation of an aqueous precursor whilst the temperature of the substrate is maintained by a hob or liquid tin bath. This leads to very slow 35 deposition rates because the growth surface is cooled substantially by the gas jet and means that low droplet fluxes must be employed to avoid excessive heat loss.

Vedel and co-workers (3) (Proc. 4th EC Photovoltaic Solar Energy Conf., Stresa [Reidel] p. 818) were the first to investigate airless atomisation for the spray pyrolysis of cadmium sulphide and showed that it led to a dramatic increase in the growth rate with a corresponding decrease in energy consumption. However, their initial results suggested that the quality of the films could be improved.

40 It has been experimentally found that the key parameter in this process is the temperature of the growth surface at the point of droplet impact and is determined by the droplet size, flux and momentum, and the available heat flux. In the preferred embodiment of the present invention, by reducing the droplet 45 size, increasing the concentration of the precursor and the heat flux, it has been made possible to increase the growth rate significantly while improving the quality of the deposited layer.

50 In the apparatus as illustrated, a Wagner Air-Coat A100 AC spray gun 30 is employed to produce an aerosol containing droplets with a quoted diameter of 8 μm with small deviation. The fan shaped nozzle 32 is used to 55 generate an elliptical droplet field across the

traverse axis of the substrate 26 which results in a more uniform temperature drop over the exposed region. The tin oxide coated glass substrate 26 rests on a partially transparent sheet of Corning 9617 ceramic plate 24 which is heated from below by a bank of tungsten halogen lamps 22. This permits direct energy input to the growing film as does the further set of lamps 33 above the substrate 26. The 70 surface temperature is measured by the optical pyrometer 36 (Omegascope 11) which controls the power input to the lower lamps 22. The position of the spray gun 30 is fixed whilst the substrate 26 executes a trochoid in 75 the horizontal plane. This arrangement produces uniform films over an area of 100 cm^2 and is limited only by the dimensions of the optical hob.

80 The optimum deposition conditions are dictated by the rate of surface cooling due to solvent evaporation and hence the maximum available heat flux. Furthermore, because of the non-availability of a nozzle with an orifice of diameter less than 125 μm , the atomisation process requires air-assistance. However, a gas jet is advantageous for acceleration of the droplets to provide sufficient velocity for maximum heat transfer after impact.

85 The most preferred method currently for depositing a cadmium sulphide layer on a substrate is effected under the following conditions:

1. Surface temperature 450°C
2. Traverse rate of hob relative to the nozzle 25 mm.s^{-1} ; Rotation rate: 5 rad.s^{-1}
3. Fluid pressure: 3 Bar (1ml.s^{-1}); Nitrogen pressure: 0.6 Bar
4. Electrode Voltage: 60KV
5. Solution Concentration: 0.15M (0.2M is possible).

100 In the photostimulated technique for the fabrication of topotaxial cuprous sulphide the cadmium sulphide layer is immersed in an organic solution of a copper salt and the exchange reaction stimulated by a light beam incident on the growth surface (see Fig. 2). The organic solution offers two advantages relative to aqueous solution. First, the cuprous state is more stable in some organic solvents and second, the solutions are transmissive over a larger range of photon frequencies, enabling different light sources to be used.

110 In the preferred embodiment, a solution of cuprous iodide in acetonitrile forces copper into a monovalent oxidation state in the complex $(\text{Cu}(\text{CH}_3\text{CN})_4)^+$, and is transmissive to CO_2 laser radiation of 940 cm^{-1} . The CO_2 laser has the advantage of a low running cost for high radiation intensities but the disadvantage of 115 poor coupling into the growth surface. The reduced power density available from incoherent visible sources is compensated for by the much greater absorbance and is a possible alternative to the CO_2 laser. It may be possible to extend this technique to the growth

of CdTe or CuInSe₂ from solution.

The exact reaction path has not been fully determined but the usefulness of the process does not of course depend on a full understanding of the chemical mechanism. It has been established that the nature of the chemical reaction is critically dependent on the dwell time. Scan rates of 2mm.s⁻¹ with a power density of 170W.cm⁻², lead to the precipitation of a thin film of copper iodide which then appears to undergo a solid phase reaction with the cadmium sulphide, the product going into solution. At scan rates of 10mm.s⁻¹ and power densities of approximately 1KW.cm⁻², experiments suggest that the reaction proceeds without precipitation of the solid. Both sets of conditions require several passes to grow a layer which is sufficiently opaque. Other combinations of cuprous and cupric salts in different solvents (e.g. pyridine and quinolene) have been attempted with varying degrees of success. Anhydrous cupric chloride dissolved in acetone produces faster growth rates but the solution possesses an absorption band at 940cm⁻¹.

It has been found that the method of deposition outlined above results in excellent crystal alignment and this has been demonstrated by X-ray diffraction spectra. This method of examination has shown that for surface temperatures less than approximately 450°C, the degree of alignment falls rapidly although the material remains hexagonal.

The chemical composition of the film has also been determined using laser mass spectrometry (LIMA2A) which has a quoted resolution of a few parts per million for most common elements. Results obtained show that the pyrolytic decomposition reaction proceeds to completion and that the only trace impurity present in detectable quantities is aluminium. This is thought to originate in a corrosion reaction within the spray gun and can be eliminated by replacing the relevant parts with stainless steel.

The electronic properties of the material have been assessed from standard electrical measurements and cathodoluminescence. The CL spectrum obtained reveals strong band edge luminescence, acknowledged to be a necessary prerequisite for efficient solar cells. The spectrum however also reveals an undesirable NIR peak whose origin has yet to be ascertained. The amplitude of this peak was found to be inversely proportional to the magnitude of the (002)/(101) peak ratio in the XRD spectrum.

Open circuit voltages from laser fabricated junctions have exceeded 550mv whilst short circuit current densities have been more difficult to ascertain since well defined contact areas were not formed in the experimental cells. Auger depth profiling has confirmed the existence of a heterojunction and is supported by complimentary LIMA spectra.

The nature of the grain boundary at the heterojunction has been investigated experimentally by exposing the cadmium sulphide layer by removal of the cuprous sulphide layer using potassium cyanide. Two junctions were evaluated in this manner, one having been prepared by the wet dip process involving the immersion of the cadmium sulphide for 5 seconds and the other produced by a CO₂ as described earlier. The results achieved both illustrate the good crystal orientation and the existence of a cuprous sulphide layer grown using the photostimulated technique.

These experimental assessments of the techniques described have confirmed the capability of producing photovoltaic devices with efficient materials usage, low energy consumption and short fabrication times.

85 CLAIMS

1. A method of forming a cadmium sulphide deposit on a transparent substrate, which comprises spraying a suitable precursor solution onto the substrate and heating the substrate to evaporate the droplets of precursor on the substrate, the substrate being heated by resting on a ceramic hob heated at least from beneath by tungsten halogen filament bulbs serving as heating elements.
2. A method as claimed in claim 1, wherein the heating elements are elongate and are fitted with reflectors to direct the energy output onto the hob.
3. A method as claimed in claim 2, wherein substrate is additionally heated by radiant energy directed onto the deposition surface from above.
4. A method as claimed in any preceding claim, wherein the hob is formed of a glass-like ceramic material.
5. A method as claimed in any preceding claim, wherein means are provided for measuring the surface temperature of the substrate and controlling the heating of the substrate to maintain the desired temperature.
6. A method as claimed in any preceding claim, wherein in order to reduce the resistance of the cadmium sulphide layer small quantities of indium are introduced into the layer by including an indium containing salt in the precursor solution.
7. A method of forming a copper sulphide/cadmium sulphide heterojunction which comprises immersing a cadmium sulphide layer in an organic solution containing a copper salt, and exposing the surface to light radiation so as to stimulate the growth of a topotaxial layer of copper sulphide on the cadmium sulphide.
8. A method as claimed in claim 7, wherein the light radiation is in the visible range and is produced by a laser.
9. A method as claimed in claim 8, wherein the laser is a carbon dioxide continuous laser and a beam produced by the laser is

scanned across the surface of the cadmium sulphide layer to stimulate the formation of the copper sulphide layer.

10. A method as claimed in claim 9,
5 wherein the laser output is pulsed or modified in time.
11. A method as claimed in claim 7,
wherein the light radiation is sunlight.

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